

CHAPTER I

THE SYNTHESIS AND TESTING OF HIGHLY STRAINED CYCLIC AND POLYCYCLIC MOLECULES AS HYPERGOLIC FUELS

Introduction

Increasing fuel efficiency has been a goal for chemists for several decades. Particularly, a more efficient fuel can increase the range of liquid-hydrocarbon-fueled ram-jets and cruise missiles.¹ A storable high-energy fuel that spontaneously ignites upon addition of an oxidizer is defined as a hypergolic fuel. Hypergolic storable fuels provide an increase in energy per unit volume of fuel and eliminate the need for an external ignition system.²

Several classes of functionalized hydrocarbons such as amines,² boranes,³ and phosphines⁴ are known to be hypergolic with nitric acid oxidizers, but only hydrazine and its simple derivatives⁵ have been found to exhibit true hypergolic behavior with H_2O_2 . Hydrogen peroxide is a good candidate for an oxidizer due to its reduced toxicity and improved storage capability. Hydrazine-based fuels are expensive, highly corrosive, and toxic, thus providing the need for investigation of other fuels that may be hypergolic with H_2O_2 .

Strained hydrocarbons have been studied as high-density fuels. Some examples including benzvalene and cubane, exhibit an increase in heat of combustion as the density of the fuel increases.¹ Many conventional hydrocarbon fuels, such as JP-5 and JP-10, show a decrease in heat of combustion as density of the fuel increases. Strained

hydrocarbons can therefore increase the range of the missile by increasing the combustion efficiency per volume of fuel.

The goal of this research is to investigate hypergolic behavior of strained hydrocarbons by adding an amine functional group which has been found to hypergolic with nitric acid oxidizers. *N,N*-Dimethyl-[3]-triangulane-7-methylamine (1), cyclopropylamines (2), cyclobutylamines (3), propylamines (4), and butylamines (5) were synthesized and investigated (Figure 1).

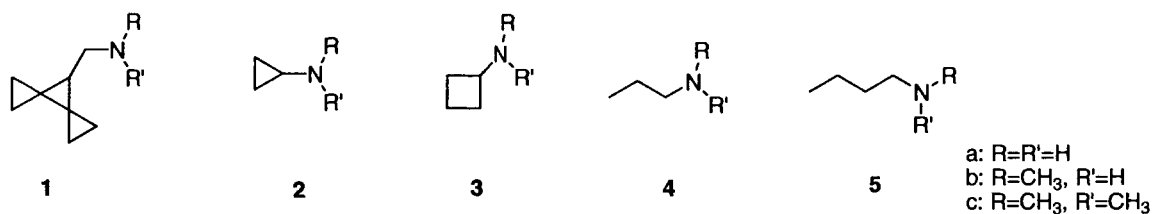


Figure 1. Amines.

The amino group should react with oxygen, providing the initiation step for ring decomposition. The highly exothermic reactions will accumulate energy and potentially lead to spontaneous ignition of the fuel. Triangulanes possess high strain energy, while the less strained cyclopropane and cyclobutanes (Table 1) are more volatile and may show shorter ignition times.